ON THE DIFFERENTIAL EQUATIONS OF BRILLOUIN-WIGNER

PERTURBATION THEORY

By

W. Byers Brown and William J. Meath

University of Wisconsin Theoretical Chemistry Institute
Madison, Wisconsin

ABSTRACT

The differential equations of Brillouin-Wigner perturbation
theory are derived directly from the Schrödinger equation.

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PERTURBATION THEORY

The Brillouin-Wigner perturbation theory was originally derived from the secular equations obtained from the spectral representation of the perturbed Schrödinger equation in terms of the solutions of the unperturbed equation[1,2,3]. This is in contrast to the Rayleigh-Schrödinger theory which is based on an expansion of the eigenvalue E and eigenfunction Ψ of the perturbed Schrödinger equation

$$\left(H_o + V - E \right) \Psi = 0 \tag{1}$$

in orders of the perturbation V. In this case the condition that the various orders are independent leads to a set of inhomogeneous differential equations. These are in general easier to solve than the original eigenvalue equation, and have received a great deal of attention recently[4,5]. The familiar spectral expansions for Ψ and E are obtained by expressing the various orders in terms of the eigenfunctions and eigenvalues of the unperturbed Hamiltonian H_o.

The object of this note is to point out that the Brillouin-Wigner perturbation theory may also be derived directly from the Schrödinger equation in a very simple way. The set of inhomogeneous differential equations obtained are of considerable interest in view of recent successful applications of the corresponding Rayleigh-

Schrödinger equations.

We begin by setting

$$\Psi = \sum_{n=0}^{\infty} \Psi^{(n)} \qquad (2)$$

where the $\Psi^{(n)}$ are not yet specified. The Schrödinger equation (1) can then be written

$$(H_0 - E)\Psi^{(0)} + \sum_{n=1}^{\infty}\left\{(H_0 - E)\Psi^{(n)} + V\Psi^{(n-1)}\right\} = 0 . \qquad (3)$$

The energy E occurring in the first term (but not in the summation) is now also expressed as an infinite sum

$$E = \sum_{n=0}^{\infty} E^{(n)} , \qquad (4)$$

where again the $E^{(n)}$ are so far unspecified. The terms in the resulting equation can be collected to give

$$(H_0 - E^{(0)})\Psi^{(0)} + \sum_{n=1}^{\infty}\left\{(H_0 - E)\Psi^{(n)} + V\Psi^{(n-1)} - E^{(n)}\Psi^{(0)}\right\} = 0 . \qquad (5)$$

We now <u>define</u> $\Psi^{(0)}$ to be a solution of the unperturbed Schrödinger equation

$$(H_0 - E^{(0)})\Psi^{(0)} = 0 \qquad (6)$$

and <u>define</u> the remaining $\Psi^{(n)}$ as the solutions of the inhomogeneous differential equations obtained by equating to zero the individual

terms of the sum in (5):

$$(H_0 - E) \Psi^{(n)} + V \Psi^{(n-1)} - E^{(n)} \Psi^{(0)} = 0, \quad n = 1, 2, \ldots \quad (7)$$

The energies $E^{(n)}$ can be obtained by multiplying (7) by $\overline{\Psi^{(0)}}$ (assumed normalized) and integrating to get

$$E^{(n)} = \langle \Psi^{(0)}, V \Psi^{(n-1)} \rangle + (E^{(0)} - E) \langle \Psi^{(0)}, \Psi^{(n)} \rangle, \quad n = 1, 2, \ldots \quad (8)$$

Since the $\Psi^{(n)}$ and $E^{(n)}$ are not completely determined by equation (7), it is natural and convenient to fix them by making all the $\Psi^{(n)}$ $(n > 1)$ orthogonal to $\Psi^{(0)}$,

$$\langle \Psi^{(0)}, \Psi^{(n)} \rangle = 0, \quad n = 1, 2, \ldots; \quad (9)$$

this is always done in conventional Brillouin-Wigner theory. Then (8) becomes

$$E^{(n)} = \langle \Psi^{(0)}, V \Psi^{(n-1)} \rangle, \quad n = 1, 2, \ldots \quad (10)$$

The nth order function $\Psi_k^{(n)}$ for a particular state k may be expanded in terms of the complete set of unperturbed eigenfunctions $\Psi_j^{(0)}$. The coefficients in the expansion can be found by multiplying (7) for the state k by $\overline{\Psi_j^{(0)}}$ and integrating to get

$$\langle \Psi_j^{(0)}, \Psi_k^{(n)} \rangle = \frac{\langle \Psi_j^{(0)}, V \Psi_k^{(n-1)} \rangle}{E_k - E_j^{(0)}}, \quad j \neq k, \quad n = 1, 2, \ldots \quad (11)$$

Successive application of this equation leads to the usual Brillouin-Wigner formula

$$\Psi_k^{(n)} = \sum_{j_1} \cdots \sum_{\substack{j_n \\ \neq k}} \frac{V_{j_1 j_2} \cdots \cdots V_{j_n k}}{(E_k - E_{j_1}^{(0)}) \cdots (E_k - E_{j_n}^{(0)})} \Psi_{j_1}^{(0)}, \quad (12)$$

where

$$V_{j_1 j_2} = \langle \Psi_{j_1}^{(0)}, V \Psi_{j_2}^{(0)} \rangle , \text{ etc.}$$

By substituting for $\Psi_k^{(n-1)}$ from equation (12) into (10) the familiar Brillouin-Wigner energy formula is obtained:

$$E_k^{(n)} = \sum_{j_1} \cdots \sum_{\substack{j_{n-1} \\ \neq k}} \frac{V_{k j_1} \cdots \cdots V_{j_{n-1} k}}{(E_k - E_{j_1}^{(0)}) \cdots (E_k - E_{j_{n-1}}^{(0)})} . \quad (13)$$

The first order Brillouin-Wigner differential equation for $\Psi^{(1)}$ has been derived previously by Young and March[6] by an operator technique. The functions $\Psi^{(n)}$ have also been derived in the reaction operator formalism by Löwdin[7], which is formally equivalent to equation (7). However, the formal inverse operator solutions of perturbation equations have not been fruitful in suggesting their realization in explicit form. It therefore seems worthwhile to focus attention on the differential equations themselves[8], and show how easily they may be obtained from the perturbed Schrödinger equation. Furthermore, the technique used is heuristic in that it suggests new perturbation schemes which are more practical than the Brillouin-Wigner and more efficient than the Rayleigh-Schrödinger.

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